

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.762:539.37

DEFORMATION OF NONFIRED COMPOSITES IN HEATING AND COOLING CYCLES

U. Sh. Shayakhmetov,¹ V. S. Bakunov,¹ V. R. Bikbulatov,¹ and I. M. Valeev¹Translated from *Steklo i Keramika*, No. 6, pp. 17 – 20, June, 2006.

The formation of nonfired ceramic composites based on aluminophosphate cement is studied depending on treatment temperature and loading. It is established that the deformation of samples tested under heating – cooling cycles varies insignificantly (even under an external load of 0.3 MPa). The resistance of cement to deformation grows if it is subjected to heat treatment at higher temperatures or to repeated testing in heating – cooling conditions.

The study of the deformation of nonfired ceramic composites under heating is a topical applied problem, since it makes it possible to develop new shrinkage-free materials, improve the technology of traditional materials, and estimate their stability in service under varying temperatures and mechanical loads. Various physicochemical processes occur in composites under heating and facilitate the formation of structures with different resistance to deformation. The technology of such products involves their pretreatment under normal conditions or in heating up to 800°C; however, their behavior under mechanical loads is not sufficiently investigated. The techniques for studying the deformation of products in such conditions have not been studied either. It is not clear which criteria should be used in developing instruments for measuring deformation in heating under a mechanic load and in choosing procedures for experiments and data processing, since available published data concern mainly fired refractories and ceramics. Therefore, the purpose of our study is to investigate the deformation of nonfired ceramic composites using the example of phosphate materials during their hardening, strengthening, and sintering depending on pretreatment temperatures. We have investigated the effect of mechanical loads in heating – cooling cycles.

For our study we selected an aluminophosphate cement composite of the composition $\alpha\text{-Al}_2\text{O}_3\text{-H}_3\text{PO}_4$ (S : L = 2 : 1) commonly used for producing fire-resistant concrete and various special-purpose materials and products [1]. It was used to produce three groups of samples molded as cy-

linders of height 76 ± 0.5 and diameter 36 ± 0.5 mm by semidry molding at 20 MPa and then exposed in air for 3 days at 20°C (the first group), preliminarily heat-treated at 300°C (the second group) or at 600°C (the third group). The deformation of samples was measured without loading or under an external mechanic load of 0.1, 0.2, and 0.3 MPa in the following heating – cooling cycles (°C): 20 – 300 – 20, 20 – 900 – 20, and 20 – 1400 – 20 (for the first group); 20 – 500 – 20 and 20 – 800 – 20 (for the second and the third groups).

In the beginning the deformation of the first group of samples was investigated. It was taken into account that cement curing occurs under heating to 300°C; moreover, its brittle failure is manifested within the temperature interval of 250 – 300°C. The choice of treatment conditions for the samples of the second and third groups was made so that the curing and dehydration processes that have a significant influence on the structure and strength parameters of cement and, accordingly, on the deformation of samples would be totally completed during preheating. These processes are related to the formation of anhydrous aluminum phosphates (the trimidite and cristobalite forms AlPO_4 and $\text{Al}(\text{PO}_3)_3$) at a temperature above 500°C, which ensures the stability of properties up to 1200°C, and the formation of a liquid phase in cement which determines its sintering.

To study impurities, we used a device developed at the BashNIPIstrom Institute based on the serial instrument, which makes it possible to perform experiments in air at temperatures up to 1550°C and load up to 5 MPa using the uniaxial compression method [1]. The experiment was carried out using the optical method for determining the linear sizes

¹ BashNIPIstrom Institute, Ufa, Russia; Institute of High Temperatures of the Russian Academy of Sciences, Moscow, Russia; Birk State Pedagogical Institute, Birk, Russia.

of the sample with a cathetometer, since this method is more precise and eliminates errors that may be caused by transmitting parts of the measuring system. The instrument sensitivity is 10 μm (0.01 mm). The sample size was determined visually through the peephole of the heating furnace by means of marks in the form of small ceramic rods of diameter 1 mm installed on the sample along its generatrix at a distance of 15 mm from its end surface. Such arrangement of the rods makes it possible to exclude the zone near the end surface of the sample experiencing nonuniform deformation under the effect of a compressive load. The main structural parameters (open porosity, apparent density) and strength parameters were determined for all samples. This made it possible to identify the trend in the sample parameter variations after various cycles depending on external loads, compared to the initial data.

All tests were performed in air by heating samples to a prescribed temperature at the rate of 4–5 K/min, then cooling at the same rate to 200°C, and finally letting them cool in the switched-off furnace.

The experimental studies of the samples of group 1 indicate (Fig. 1) that under heating to 200–250°C a slight shrinkage occurs in hardening, i.e., a decrease in the cement sample sizes, which decelerates, and then the curves exhibit a certain expansion, most probably of thermal origin. This deformation is caused by the formation of acid phosphates in the cement composite and shrinkage in drying. Loading a sample increases its shrinkage, i.e., the compaction of cement is accompanied by its viscous flow under a load. With increasing temperature and the loss of free water, compression slows and is replaced by the thermal expansion of the emerging skeleton of solid particles of acid aluminum phosphates. The residual deformation observed depends on the load applied. The cooling curves are mainly rectilinear. The CLTE of samples is virtually identical (approximately $5 \times 10^{-6} \text{ K}^{-1}$) as the angle of the cooling curves is constant and not affected by the degree of deformation in heating.

The expansion of a sample in the 20–900–20°C cycle also starts at a temperature around 300°C (Fig. 2a). The cristobalite form AlPO_4 in cooling presumably undergoes a polymorphic transformation at a temperature below 200°C; accordingly, a slight inflection is seen on the curve. The CLTE does not vary.

In the 20–1400–20°C cycle we observe the plastic deformation of cement in the curve above 1000°C caused by its flow; the residual deformation is about 2% (Fig. 2b).

When the cement composite is cooled without loading, in the temperature interval of 160–190°C the sample compression rate changes, caused by the reverse transition of AlPO_4 from its high-temperature α -modification to the low-temperature β -modification.

A more steady shrinkage and deformation process is observed in cement samples of groups 2 and 3, which are preliminarily heat-treated at temperatures of 300 or 600°C, respectively.

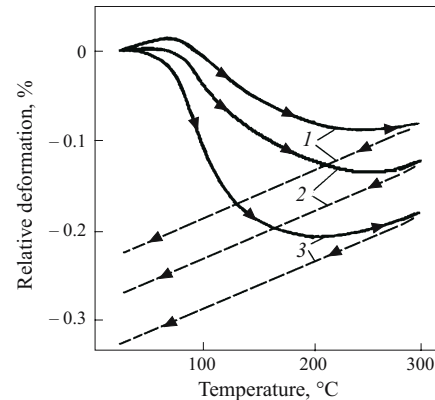


Fig. 1. Deformation of $\alpha\text{-Al}_2\text{O}_3\text{-H}_3\text{PO}_4$ composite (samples of group 1) in cycle 20–300–20°C without loading (1) and under loading of 0.1 (2) and 0.2 MPa (3).

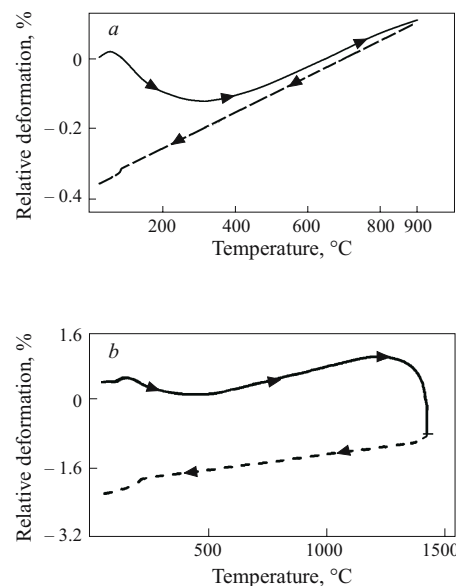


Fig. 2. Deformation of $\alpha\text{-Al}_2\text{O}_3\text{-H}_3\text{PO}_4$ composite (sample of group 1) in cycle 20–900–20°C (a) and 20–1400–20°C (b) without loading.

Comparing the deformation curves of two groups of samples in heating–cooling cycles of 20–500–20 and 20–800–20°C (Figs. 3 and 4) experiencing a load of 0.3 MPa and the deformation curves after repeated heating–cooling cycles without loading, it can be noted that an external load contributes to the compaction of cement and thus makes it possible to eliminate residual deformation under repeated heating without loading. Furthermore, the curves of deformation under loading have no inflection in the range of 150–250°C, which indicates the prevalence of deformation over expansion.

The data on the relative and residual deformation of samples of groups 2 and 3 after testing in 20–500–20 and 20–800–20°C heating–cooling cycles are given in Table 1.

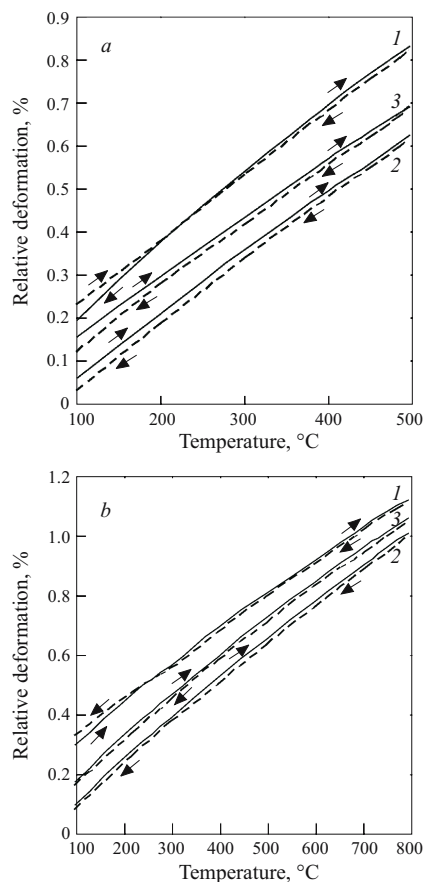


Fig. 3. Deformation of samples of group 2 (heat-treated at 300°C) in cycles 20 – 500 – 20°C (a) and 20 – 800 – 20 (b): 1) without loading; 2) under loading of 0.3 MPa; 3) repeated cycle without loading after testing under a load of 0.3 MPa.

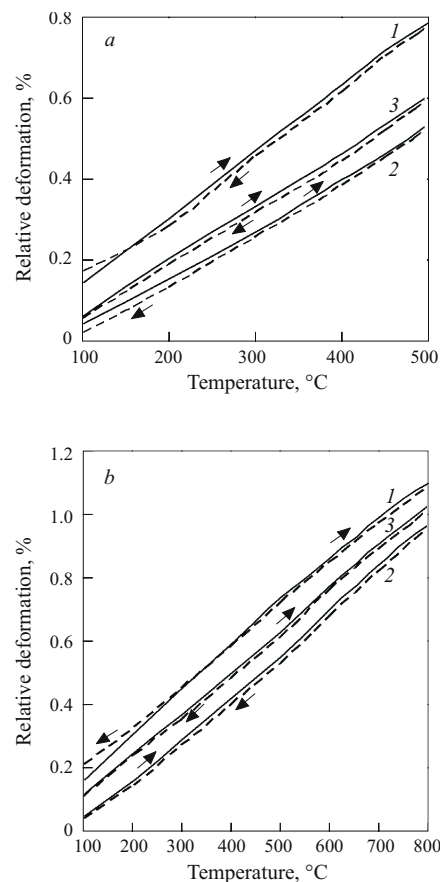


Fig. 4. Deformation of samples of group 3 (heat-treated at 600°C) in cycles 20 – 500 – 20°C (a) and 20 – 800 – 20 (b): 1) without loading; 2) under loading of 0.3 MPa; 3) repeated cycle without loading after testing under a load of 0.3 MPa.

The study of the deformation of samples of the third group in heating – cooling cycles (heat treatment temperature 600°C) indicate (Fig. 4) that preliminary heat treatment

of cement at 600°C instead of 300°C (group 2) makes it possible to exclude or substantially lower the residual deformation of cement in 20 – 500 – 20 and 20 – 800 – 20°C cycles.

TABLE 1

Group of samples	Testing conditions	Deformation, %		Testing conditions	Deformation, %	
		relative	residual		relative	residual
Second	Primary cycle 20 – 500 – 20°C: without loading	0.82	0.10	Primary cycle 20 – 800 – 20°C: without loading	1.10	0.11
	under loading, MPa:			under loading, MPa:		
	0.1	0.75	– 0.02	0.1	1.09	0.03
	0.2	0.67	– 0.06	0.2	1.07	– 0.07
	0.3	0.62	– 0.10	0.3	1.01	– 0.13
Third	Cycle without loading after primary cycle under load of 0.3 MPa	0.69	0.02	Cycle without loading after primary cycle under load of 0.3 MPa	1.03	0.02
	Primary cycle 20 – 500 – 20°C: without loading	0.78	0.03	Primary cycle 20 – 800 – 20°C: without loading	1.10	0.05
	under loading, MPa:			under loading, MPa:		
	0.1	0.65	–	0.1	1.01	0.03
	0.2	0.59	– 0.03	0.2	0.99	– 0.02
	0.3	0.53	– 0.07	0.3	0.97	– 0.06
	Cycle without loading after primary cycle under load of 0.3 MPa	0.60	–	Cycle without loading after primary cycle under load of 0.3 MPa	1.06	0.01

TABLE 2

Samples	Open porosity, %	Apparent porosity, g/cm ³	Compressive strength, MPa
Initial (treatment temperature 300°C)	32.0	1.77	27.6
After cycle:			
without loading	32.2	1.77	28.8
with loading, MPa:			
0.1	33.1	1.78	30.1
0.2	33.0	1.78	34.3
0.3	32.9	1.79	39.4

A certain increase in the density and compressive strength of cement is observed after deforming under a load of 0.1, 0.2, and 0.3 MPa, which points to the evolution of its structure at heat treatment under an external mechanical load. The properties of samples tested in 20 – 500 – 20 cycle are listed in Table 2.

It is also established that the strength of samples grows under an increasing load when the cement treatment temperature is raised from 300 to 600°C, which is related to a certain stabilization of their structure. The porosity in this case decreases to some extent and the density grows, which is quite natural, since the external force contributes to the production of cement with a dense and more deformation-resistant structure. This is facilitated by the completion of the dehydration process.

Judging by the analysis of the physicommechanical characteristics of cement composite samples before and after treatment when heated to 1500°C, we can state that at a temperature above 1300°C their strength increases (Fig. 5), which is determined by the sintering of the composite.

The density of cement significantly grows at temperatures above 1200°C (without loading) and under a load the compaction is more perceptible and occurs at lower temperatures. At the same time, porosity perceptibly decreases starting with 1300°C.

Thus, the deformation of samples tested in heating and cooling vary insignificantly (even under an external load of

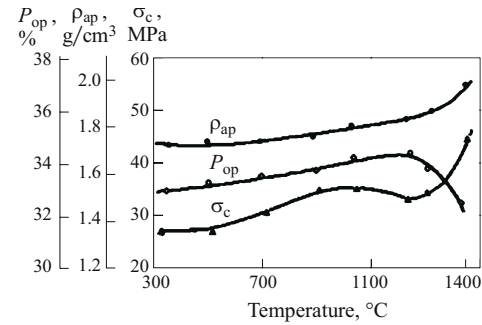


Fig. 5. The effect of treatment temperature on compressive strength σ_c , open porosity P_{op} , and apparent density ρ_{ap} .

0.3 MPa). Composites obtained by semidry molding are resistant to deformation under loading when heated up to 900°C. Insignificant shrinkage (up to 0.2%) is observed only under primary heating up to 250 – 300°C. All modifications in cement tested in heating – cooling conditions are mainly caused by the redox and adhesion processes, whereas an externally applied load does not have a significant effect on its phase and structural modification; accordingly, the deformation of cement is minimal. The resistance of cement to deformation grows if it is heat-treated at a higher temperature or subjected to a repeated heating – cooling testing, which has an important practical significance, as such cement can be used to produce shrinkage-free ceramics and refractories.

Testing in the 20 – 1400 – 20°C cycle indicates the significant role of the viscous flow in the temperature range above 1000°C. In this case, even without loading, the deformation of the sample is substantial. The residual deformation of this cement tested after 3 days of exposure in air is about 2% (without loading); under loading it increases to 5%.

REFERENCES

1. U. Sh. Shayakhmetov and A. G. Mustafin, *Specifics of High-Temperature Creep in Nonfired Ceramics* [in Russian], Khimiya, Moscow (2005).